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SPRAY-DRIED SODIUM-POTASSIUM BETA/BETA"-ALUMINA

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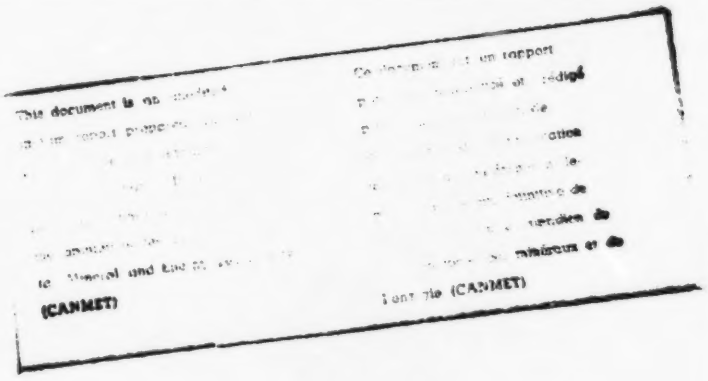

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SPRAY-DRIED SODIUM-POTASSIUM BETA/BETA"-ALUMINA

by

A.K. Kuriakose*, T.A. Wheat*, A. Ahmad* and J.D. Canaday*

ABSTRACT

This paper describes the newly discovered effects of MgO content and particle size of the alumina raw material in yielding a sodium-potassium beta/beta"-alumina of high beta"-content when the reactants are spray-dried from a slurry. It also deals with the influence of the total MgO on the beta"- content of the prod[illegible] and the effect of Li_2O as a sintering aid.

The beta"-alumina [illegible]tent of the 60 mol% Na_2O:40 mol% K_2O beta-alumina precursor powder is substantially increased (from about 25% to about 50%) when as little as 0.2 wt% of MgO is prereacted with the alpha-alumina reactant of specific particle sizes. The effect is not observed when a coarse form of alpha-alumina (>5 μm) or extremely fine (<1 μm) gamma type alumina is used.

The beta"-alumina content of the 0.60Na/0.40K composition increases markedly with an increase of MgO content in the system up to about 1.3 moles of MgO per mole of the material. However, these high MgO compositions cannot be sintered into high density form by the standard sintering technique. The inclusion of a small amount of Li_2O in the compositions aids the sintering process remarkably; but the Li_2O in the system tends to reduce the beta"- content. This latter effect is opposite to that observed in the synthesis and sintering of pure sodium beta"-alumina.

This study represents part of the work on the Hydrogen-Air Fuel Cell Program carried out at CANMET; the objective of this element of work has been the development of an industrially acceptable process for the manufacture of sodium-potassium beta-alumina of high beta"-content, which is essential for the preparation of the hydrogen ion conducting membrane slated for the CANMET-designed solid-state hydrogen-air fuel cell. The process described here is suitable for industrial production.

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ALUMINE BÊTA/BÊTA" SODIQUE-POTASSIQUE SÉCHÉE PAR ATOMISATION

par

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RÉSUMÉ

Les auteurs de ce rapport rendent compte des effets, nouvellement découverts, de la teneur en MgO et de la granulométrie du minerai sur la production d'une alumine bêta/bêta" sodique-potassique à forte teneur en bêta" lorsque les réactifs, à l'état de boues, sont séchés par atomisation. Ils décrivent aussi l'influence de la teneur totale en MgO sur la teneur en bêta" du produit, ainsi que les propriétés agglomérantes de Li_2O.

La teneur en alumine de type bêta" de la poudre dans laquelle Na_2O et K_2O sont présents dans un rapport moléculaire de 60/40 augmente considérablement (d'environ 25 % à près de 50 %) lorsqu'au préalable, à peine 0,2 % (en poids) de MgO est mis en présence d'un réactif à alumine réduit à la taille voulue. Cet effet est absent lorsque l'on utilise de grosses particules d'alumine alpha (~5 µm) ou une alumine gamma extrêmement fine (<1 µm).

La teneur en alumine bêta" de la composition à 60 % de Na et 40 % de K s'accroît de façon nette quand on augmente la teneur en MgO du système à environ 1,3 mole de MgO par mole de matière première. Cependant, la technique d'agglomération classique ne permet pas d'augmenter considérablement la densité de ces compositions à forte teneur en MgO. Si l'adjonction d'une faible quantité de Li_2O améliore l'agglomération d'une façon remarquable, la présence de ce composé dans le système a tendance à réduire la teneur en bêta". C'est le contraire de ce qui a été observé dans la synthse et l'agglomération de l'alumine bêta" sodique pure.

Cette étude s'inscrit dans le cadre du Programme de recherches sur les piles à combustibles à hydrogène-air poursuivi à CANMET. Elle a pour but de mettre au point un procédé industriel de fabrication d'alumine bêta sodique potassique à haute teneur en bêta", produit essentiel à la préparation de la membrane conductrice d'ions d'hydrogène qui est destinée à la pile à combustibles hydrogène-air à semi-conducteurs conçue par CANMET. Le procédé décrit dans ce rapport convient à une production industrielle.

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INTRODUCTION

As is well known, fuel cells are the most efficient energy conversion devices as they convert chemical energy directly into electricity. The high efficiency of fuel cells arises from the absence of the Carnot cycle in their operation, contrary to thermomechanical conversion devices such as heat engines. Several types of fuel cells are known, but a low temperature (≈300°C) solid state hydrogen-air fuel cell appears to be the most desirable, based on its advantages over the others (1).

Hydrogen or hydronium ion conducting beta/beta"-alumina is an attractive membrane material for the low temperature solid state hydrogen-air fuel cell. This material can be prepared in single crystal form by simple ion exchange of their sodium conducting analogues, also in single crystal form (2). But such single crystals are not large enough to be utilized in power devices such as fuel cells. On the other hand, polycrystalline sodium beta/beta"-alumina disintegrates on hydronium ion exchange due to the anisotropy in expansion of the sodium ion conductor on ion displacement by the 40% larger hydronium ion. However, if potassium beta/beta"-alumina can be prepared, it can be ion exchanged by hydronium ions without break-down, because potassium and hydronium ions match very closely in size. Direct synthesis and sintering of pure potassium beta"-alumina have so far not been successful due to he unstable nature of the product at the high tempeatures (≈1600°C) required for the sintering. A successful route to the fabrication of potassium beta"-alumina has been the ion exchange of the sodium analogue by the use of potassium vapour at high temperatures (3). However, this procedure is difficult because of the need for handling potassium vapour. Potassium ion exchange of the pure sodium compound in molten potassium nitrate bath has been tried, but is not satisfactory due to deterioration of the material at the molten KNO_3 temperature of 350°C (4).

Work at McMaster University (5) has shown that the maximum proportion of potassium that can be incorporated into sodium-potassium beta alumina is about 40 mol% of the total alkali fraction in order to obtain any significant amounts of beta"-alumina in the product after sintering. They have also shown that such mixed ion products can be fully exchanged into the potassium form by ion exchange in a molten KCl bath. Studies at

Queen's University (6) have indicated that the bulk ionic conductivity of sodium-potassium beta alumina is enhanced dramatically (by about three orders of magnitude) when the f(beta) value of the product is reduced to less than about 0.37. The objective of the present study was to fabricate sintered products of sodium-potassium beta/beta"-alumina with a potassium content of 40 mol% in the alkali fraction and an f(beta) value of 0.37 or less. A commercially desirable spray-drying process was investigated for the system so that any developed technology could be transferred to industry with minimum of developmental work. This would provide the precursor material required for the synthesis of highly conducting hydronium beta/beta"-alumina for use as membranes in a hydrogen-air fuel cell that is being developed.

EXPERIMENTAL PROCEDURES

Reagents: The reagents used in making the compositions were: anhydrous sodium carbonate, anhydrous potassium carbonate, aluminum oxide (RC-172, C-71 and also a sample synthesized by the decomposition of aluminum sulphate), magnesium oxide or acetate, lithium carbonate or acetate.

Procedure: In the preliminary work, the ingredients were ground together into a paste with drops of distilled water in an alumina mortar with alumina pestle, the paste was dried in an air oven at about 110°C and the resulting powder was calcined at a temperature of typically 1250°C for 30 min. An X-ray diffraction pattern of the calcined powder was obtained and the f(beta) of the product was calculated from the relationship:

$$f(\text{beta}) = I(\text{beta})/[I(\text{beta}) + 1.37\ I(\text{beta}")]$$

where I(beta) and I(beta") are respectively the intensities of the X-ray diffraction peaks of beta- and beta"-aluminas corresponding to the d-spacings of 0.269 and 0.260 nm respectively (7).

In the case of MgO-doping experiments on alumina, the alumina was mixed with the required amounts of MgO or magnesium acetate and ground into a paste as before and calcined at 1250°C.

Aluminum oxide of extreme fineness was prepared by the thermal decomposition of aluminum sulphate crystals. At temperatures below 1000°C, the product was mostly gamma-alumina. It was further heat-treated at 1100, 1200, 1250, 1300 and 1400°C in order to recrystallize the material to the coarser alpha-alumina form. These samples were further doped with MgO as required, by the procedure described above.

After obtaining a satisfactory low f(beta) value on the beta-alumina product by calcination, that particular composition was prepared on a larger scale by the spray-drying method. First, carbon dioxide was bubbled through a solution of sodium and potassium carbonate, the required amount of MgO was added and carbon dioxide was passed through again until a clear solution was obtained. Calculated amounts of aluminum oxide were added to the resultant solution and the mixture was shaken in a plastic bottle containing alumina balls for 30 min in order to break up aggregates. The slurry thus obtained was filtered through a 60 mesh screen and spray-dried in a Buchi lab unit at an inlet temperature of about 220°C and an outlet temperature of about 130°C. Aliquots of the powders were calcined at various temperatures in order to ascertain the optimum temperature of calcination for obtaining a powder with the lowest f(beta) value as determined by X-ray diffraction.

In another procedure, the carbonates of sodium, potassium, and magnesium were dissolved in acetic acid instead of the bicarbonate preparation and alumina was then added as before to make the slurry for spray-drying.

After calcination at the selected temperatures, the samples were uniaxially pressed into discs of about 1.2 cm diameter and 3 mm thickness in a steel die at a pressure of about 140 MPa. The discs were then sintered at temperatures ranging from 1600 to 1650°C for 5 to 15 min in a closed platinum crucible, using powder of the same composition for packing. The densities of the discs were determined by measuring the diameter, thickness and weight of each disc. The f(beta) values of the fired discs were measured as before by X-ray diffraction and peak intensities of the beta- and beta"-forms.

RESULTS

THE EFFECT OF MgO ON THE YIELD OF BETA" PHASE IN THE SODIUM POTASSIUM MIXED COMPOSITION

The effect of MgO as a stabilizer for beta"-alumina with 60 mol% Na_2O and 40 mol% K_2O was studied using RC-172 alumina as the alumina source. The other reactants were sodium carbonate, potassium carbonate and magnesium oxide. Approximately 80-g batches of the compositions were prepared by spray-drying as described earlier. The f(beta) of the various compositions was determined after calcination at temperatures ranging from 800°C to 1400°C and also after sintering some of these calcined compositions. The results of these experiments are shown in Table 1. It is clear that no beta"-alumina is formed until the calcination temperature is at least about 1100°C, although small amounts of beta-alumina are produced even at 800°C. The highest proportions of the beta"-phase are formed at temperatures of 1250 to 1350°C at all MgO concentrations. Although MgO contents of both 0.7 and 1.3 mole/mole produce powders of similar beta"-content, on sintering only the 1.3 MgO composition yields a product rich in beta"-phase. The f(beta) of the 0.7 MgO composition increases on sintering. An MgO content of 1.3 yields a product which has a f(beta) of even less than the required 0.37. A high MgO content of 1.3 thus has a very strong stabilizing effect on the beta"-phase in the 0.60 Na/0.40 K beta-alumina composition. It is not clear why an intermediate MgO content of 1.0 yields a product that has an even higher f(beta) than the 0.7 MgO composition, on calcination.

THE EFFECT OF THE TYPE OF ALUMINA ON f(Beta)

(1) High Purity Alumina Prepared from Aluminum Sulphate:

The purpose of using high purity alumina was to prepare very high purity beta/beta"-alumina and to investigate the effect of the particle sizing and the type of alumina phase (e.g., gamma and alpha aluminas) on the yield of sodium-potassium beta/beta"-alumina. To achieve this, the alumina was prepared by thermally decomposing aluminum sulphate and calcining the sulphate decomposition product at 900, 1200, 1250 and 1400°C. The 900°C and the 1200°C calcines contained practically no alpha-alumina as found by X-ray diffraction. Mixtures were prepared using

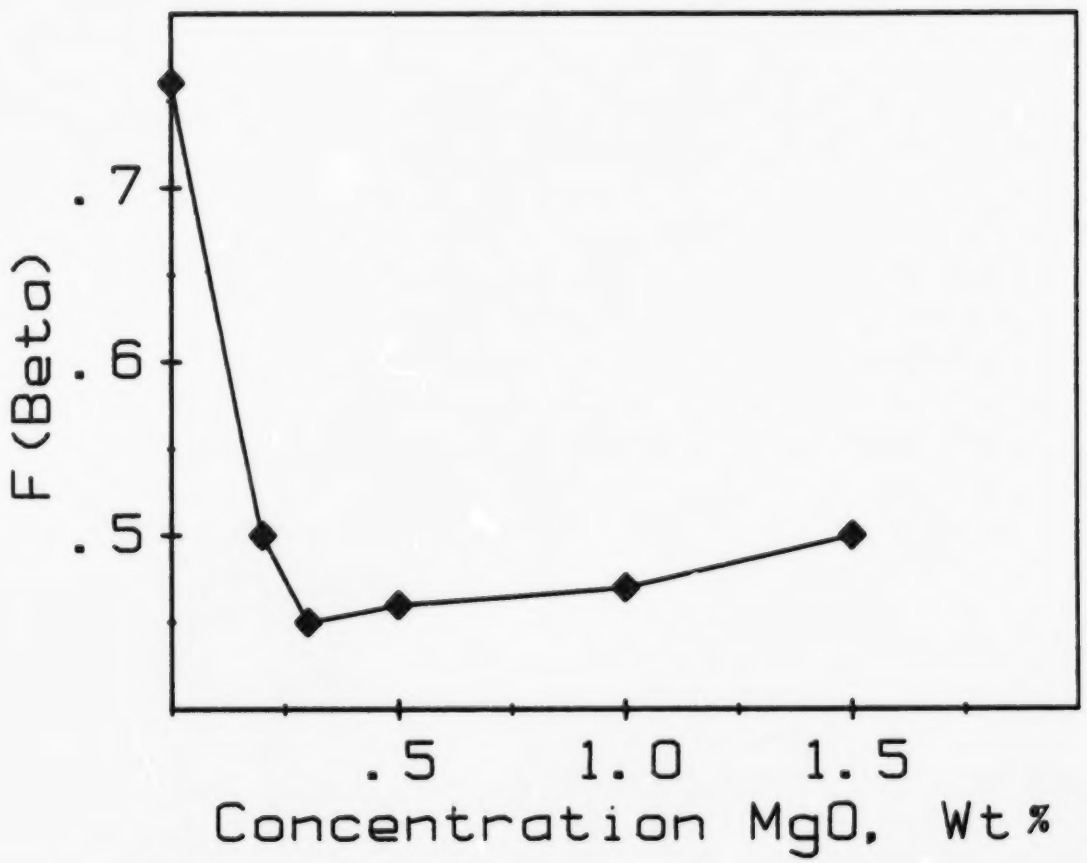

Fig. 1 - The effect of doping alpha-alumina with MgO on the f(beta) of powder

each sample of these aluminas to make 0.60 Na_2O:0.40 K_2O:1.3 MgO:6.0 Al_2O_3 compositions and then calcined at 1250°C for 30 min as listed in Table 2. It is obvious that the gamma-type alumina does not produce beta"-alumina when the reactants are calcined at 1250°C. On the other hand, the production of beta"-phase is related to the presence of alpha alumina in the reactants - more beta"-phase is formed when higher amounts of alpha-alumina are present. Also, coarser crystals of alpha-alumina tend to produce more beta"-phase, as indicated by the production of more beta"-phase from alumina calcined at higher temperatures.

(2) RC 172 Alumina:

This is a finely divided alpha alumina with a particle size range of < 2 μm. It is known to be excellent for many sintering applications in producing high-density high alumina bodies. The use of RC-172 alumina in making 0.60 Na_2O/0.40 K_2O:1.3 MgO:6.0 Al_2O_3 yielded a product with an f(beta) of 0.33 on calcination at 1250°C for 1 h. Thus, RC-172 is much more efficient than high purity aluminum oxide (prepared from aluminum sulphate) in producing mixed Na/K beta"-alumina. The reason for this behaviour could be the presence of a small amount of MgO (≈0.2 wt %) in the RC-172. In order to verify this theory, the effect of adding MgO to the high purity alumina and calcining it prior to making the Na/K beta-alumina was investigated.

Pure aluminum oxide calcined at 1400°C was used for these tests. Varying proportions of MgO ranging from 0-2 wt % of the alumina were mixed with the alumina and calcined at 1250°C for 30 min. (Magnesium acetate was used as the MgO source for these experiments). The resulting powders were first subjected to X-ray diffraction analysis for phase content and then incorporated into mixtures for the synthesis of 0.60 Na_2O/0.40 K_2O: 1.3 MgO:6.0 Al_2O_3 beta/beta"-alumina. Alumina-MgO calcines with less than 0.5 wt % contained no detectable amounts of spinel; traces of spinel were found at the 0.5% level and these increased with further increase in the MgO content. The variation of the f(beta) with the change in the MgO content of the alumina is illustrated in Table 3 and Fig. 1. As little as 0.2 wt % of MgO in the alumina has a significant effect on the f(beta); the lowest f(beta) (highest beta"-phase) is obtained after calcination at 1250°C at 0.3-0.5 wt % of MgO.

(3) C-71 Alumina:

The crystal size of C-71 alumina is approximately 5 μm. This is alpha alumina in a considerably coarser form than the others used in this study. In one experiment, the Na/K composition was prepared and calcined using the untreated C-71 powder. In another, the C-71 was first heat-treated with 0.3% by weight of MgO before making the Na/K beta mixture. After calcination at the usual 1250°C for 30 min, f(beta) values respectively of 0.34 and 0.36 were obtained with the undoped and doped materials. This shows that when the alpha alumina is coarse (5 μm), MgO-doping has no effect on the subsequent yield of Na/K beta"-alumina. However, highly desirable low f(beta) values are obtained even without any doping, using C-71 alumina.

SINTERING OF THE POWDERS

The various calcined powders were pressed into discs, which were sintered at 1650°C for 5 min. Table 4 gives the density and f(beta) values of these samples. It is clear that the doped alumina, RC-172 and C-71 all yield products with an acceptable f(beta) value; but none of them has an acceptable density. Several attempts were made to improve the sintered dnesity by changing the sintering conditions of temperature and time, but no significant improvement in the density could be obtained. It was therefore necessary to consider a sintering aid for these compositions. Li_2O is known to be a sintering agent for several oxide ceramics and hence it was decided to study its influence on the sintering behaviour of the mixed sodium/potassium beta-alumina compositions. RC-172 was selected as the raw material alumina for these studies. Varying levels of Li_2O were incorporated, in the form of lithium carbonate or lithium acetate, into the composition before spray-drying of the reagents. After calcination, the various mixtures were pressed into discs and were sintered at 1625°C for 10 min. The results of these experiments are displayed in Table 5. The sintered density is clearly improved by the presence of Li in the system. Although the density of the product increases at least up to 0.3 mole of Li_2O per mole, about 0.15 mole/mole is sufficient to obtain approximately 96% sintered density. The f(beta) of the sintered product, however, is

increased by the incorporation of the Li_2O. This is in contrast to the effect of Li_2O in the synthesis of sodium beta"-alumina, where it is used as a beta"-alumina stabilizer. An increase of Li_2O content from 0.05 to 0.30 mole/mole, nevertheless, does not reduce the beta"-content of the sodium-potassium beta-alumina. The absence of MgO in the system even when the Li_2O is present reduces the beta"-phase content. This again shows that in the Na/K beta-alumina system, MgO is a stabilizer for the beta"-form, but Li_2O is not.

Because the use of C-71 alumina produced the highest beta"-alumina content of all the alumina raw materials tried, attempts were made to increase the sintered density of the C-71 product by using Li_2O as sintering aid. Three levels of Li_2O concentrations, with or without MgO stabilizer, were tried. However, Li_2O failed to show its role as a sintering aid in these cases and the beta"-phase content of the product decreased considerably with the increase in the Li_2O concentration. Table 6 illustrates these points.

The foregoing experiments indicated that RC-172 alumina was the preferred alumina starting material from among the three alumina materials examined, for the fabrication of Na/K beta-alumina of high density and high beta"-alumina content. Hence batches of Na/K beta-alumina powder compositions were prepared by spray-drying slurries made with RC-172 alumina containing Li_2CO_3 and the other ingredients either in the form of bicarbonates or acetates. A Li_2O concentration of 0.15 mole/mole was used for these preparations. Determination of f(beta) after calcination of 2-g samples of the powder at various temperatures ranging from 900 to 1400°C for 30 min revealed that calcination at 1300°C produced the powder with the lowest f(beta) of about 0.35. At 900°C no beta"-alumina was present, but at 1100°C an f(beta) of about 0.5 was found. No significant differences were observed between the bicarbonate and the acetate processes. The powders were sintered at 1625°C for 10 min in the form of discs and the results obtained are recorded in Table 7. The sintered densities and the f(beta) values were excellent.

DISCUSSION

MgO-DOPING OF THE RAW MATERIAL ALUMINA

The effect of MgO-doping of the reactant alumina on the yield of beta"-alumina has not been reported before. This effect was discovered through the use of either RC-172 alumina or high purity alumina for the Na/K alumina-synthesis. It was observed that the RC-172 invariably yielded more beta"-alumina when processed with the other reagents although the high purity alumina sample was a more reactive form of alumina from a surface area point of view. Even when the two types of alumina with equivalent surface areas were used for the preparation, the RC-172 yielded more beta"-product. Because the high purity alumina was prepared by the thermal decomposition of high purity aluminum sulphate in platinum vessels, no contamination was present. On the other hand, the reported chemical analysis of RC-172 alumina shows the presence of small amount of MgO in the material. Hence experiments were carried out on the system by doping the pure alumina with MgO. Although no significant effect of the doping of the extremely fine gamma type alumina is found on the beta"-phase production, the coarser alumina in the alpha form formed by higher temperature calcination does reveal a significant influence. Despite this effect, alpha alumina coarser than 5 μm does not show any special influence by MgO. The effect of MgO may be attributed to some degree of strain in the alpha alumina crystals. When the crystals are large, even without any MgO, strain will be present.

THE EFFECT OF MgO CONCENTRATION

In the case of pure sodium beta-alumina prepared by aqueous spray-drying, about 0.8 mole of MgO per mole is sufficient for the stabilization of the beta"-alumina. However, as potassium substitutes the sodium, the MgO requirement increases considerably for the beta"-form stabilization. Thus, for the 0.6 Na_2O:0.4 K_2O:6.0 Al_2O_3 composition, 1.3 mole of MgO per mole is required to obtain an f(beta) value less than about 0.37 after sintering. It is not clear why such a high proportion of MgO is needed when 40 mol% of the sodium is substituted by potassium. In addition to the instability of the potassium beta"-alumina, it appears to have a destabilizing effect on the sodium beta"-alumina. An excess of MgO compensates for this destabilizing effect.

It is interesting that even in presence of 1.3 moles of MgO, no beta"-alumina is formed when the reactants are calcined at 900°C. the formation of beta"-alumina starts at temperatures of about 1100°C and the highest proportions of beta"-phase are formed at 1250-1350°C. It is therefore inferred that the formation of beta"-alumina has a higher activation energy than that for the beta-form, or the alumina raw material has to be in the alpha form for the beta"-formation. Beyond 1400°C again the proportion of beta"-phase decreases, which is to be expected because the potassium beta"-alumina becomes unstable above that temperature as reported by Nagai et al. (7).

SINTERING OF THE POWDERS

It is not clear why the compositions that yield satisfactory beta"-content do not sinter under various conditions of temperature and time. It appears that either there is no liquid phase formation in the Na_2O-K_2O-MgO-Al_2O_3 system under the sintering conditions tried, or that the vapour pressure in the system is too high for densification. The presence of lithia in the system, however, helps the sintering remarkably, although with a drop in the beta"-alumina content of the sinter. Again it is not clear why the lithia does not act as a beta"-stabilizing agent as it does in the sodium beta"-alumina. SEM studies show an increase in the grain boundary phases and it is to be assumed that the lithia stays mainly in these grain boundary phases rather than in the crystal lattice. Unfortunately, EDAX does not detect Li and hence this assumption cannot be easily proved. Nevertheless, a sintered 0.6 Na/0.4K beta-alumina of acceptable density and f(beta) can be fabricated by the process described.

It is noteworthy, in Table 6, that a sintered 0.6 Na/0.4K product with an f(beta) value of 0.18 can be prepared using the coarse C-71 alumina for the synthesis in the absence of lithia. Although the product has a low density after sintering at 1625°C the very low f(beta) of 0.18 shows that potassium beta"-alumina can exist at 1625°C, contrary to the theory proposed by earlier workers (5,6).

CONCLUSIONS

A sodium-potassium beta/beta" alumina containing 60 mol% Na_2O and 40 mol% K_2O in the alkali fraction can be synthesized and sintered to densities over 95% of theoretical with an f(beta) value of less than 0.37 by using a spray-drying process for the preparation of the precursor powder. An MgO content of 1.3 mole/mole as a beta"-alumina stabilizer and a lithia content of 0.15 mole/mole as a sintering aid are required in the system for the process. A slurry of RC-172 alumina or alpha alumina of crystal size about 2 μm that is doped with at least 0.2 wt % MgO, prepared with the remaining reactants in an aqueous bicarbonate or acetate solution mixture can be used for the spray-drying.

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Table 1 - The effect of MgO on the yield of beta"-alumina in 60/40 Mixed Na/K compositions*

Calcination Temp. °C	MgO Content mole/mole	f(beta) calcine	f(beta) sinter
800	0.7	1.0	
	1.0	1.0	
	1.3	1.0	
1000	0.7	1.0	
	1.0	1.0	
	1.3	1.0	
1100	0.7	0.48	
	1.0	0.53	
	1.3	0.46	
1200	0.7	0.42	
	1.0	0.52	
	1.3	0.42	
1250	0.7	0.39	0.65
	1.0	0.45	0.61**
	1.3	0.39	0.29
1300	0.7	0.42	
	1.0	0.50	
	1.3	0.40	
1350	0.7	0.38	
	1.0	0.47	
	1.3	0.41	
1400	0.7	0.47	
	1.0	0.51	
	1.3	0.39	

* Basic composition: 0.6 Na_2O:0.4 K_2O:6.0 Al_2O_3; Alumina used: RC-172

**Powder calcined at 900°C

Table 2 - The effect of precalcination temperature of alumina on the yield of beta"-alumina

Calcination Temp. °C	Al_2O_3 Type	f(beta) of Product
900	gamma	1.00
1200	gamma	1.00
1250	gamma + tr alpha	0.90
1400	alpha	0.75

Table 3 - The effect of the extent of MgO-doping* on the f(beta) of product

MgO Doping (Wt %)	f(beta) of Product
0.0	0.75
0.2	0.50
0.5	0.45
1.0	0.47
1.5	0.51
2.0	0.48

*Al_2O_3: Prepared from aluminum sulphate and calcined at 1400°C; MgO: Added as magnesium acetate; Doping and calcination at 1250°C.

Table 4 - Density and f(beta) of products obtained using various Al_2O_3 raw materials*

Alumina Sample	Green		Sintered	
	Density	f(beta)	Density	f(beta)
From $Al_2(SO_4)_3$ at 1300°C undoped	1.66	0.45	2.10	0.40
From $Al_2(SO_4)_3$ doped with 0.5 wt % MgO	2.01	0.37	1.99	0.33
RC-172	1.74	0.28	2.70	0.29
C-71 undoped	2.16	0.35	2.13	0.18
C-71 doped with 0.5 wt % MgO			1.93	0.31

*Composition: 0.6 Na_2O:0.4 K_2O:1.3 MgO:6.0 Al_2O_3;
Calcination temp: 1250°C/30 min;
Sintering at 1650°C/5 min.

Table 5 - The effect of Li_2O content on the f(beta) and sintered density of Na/K beta alumina*

Li_2O Concentration mole/mole	Green		Sintered	
	Density	f(beta)	Density	f(beta)
0.05	1.99	0.52	2.81	0.48
0.10	2.05	0.40	2.97	0.38
0.15	1.84	0.40	3.14	0.48
0.20	1.96	0.42	3.15	0.46
0.30	1.85	0.55	3.22	0.46
0.15**	1.93**	0.71**	3.18**	0.87**

* Reactants: RC-172 Alumina; Lithium carbonate; Magnesium oxide; Sodium carbonate and potassium carbonate; Method: Hand-mixed paste; Calcination Temp: 1250°C/30 min; Sintering at 1625°C/10 min.

**No MgO in mix

Table 6 - The effect of Li_2O on the sintering of Na/K beta-alumina made with C-71 alumina*

Li_2O Concn.	MgO Concn. (mole)	f(beta) (powder)	Sint. Density	Sint. f(beta)
0.00	1.3	0.35	1.97	0.18
0.05	1.3	0.40	2.14	0.27
0.10	0.0	0.55	2.38	0.87
0.20	1.3	0.53	2.46	0.41
0.30	0.0	0.64	2.11	0.87

*Method: Hand-mixed paste; Composition: 0.6 Na_2O:0.4 K_2O:6.0 Al_2O_3

Table 7 - Sintered densities and f(beta) of spray-dried 0.6 Na_2O:0.4 K_2O::1.3 MgO:6.0 Al_2O_3:0.15 Li_2O compositions**

Slurry Type	f(beta) (powder)	Green Density	Sintered	
			Density	f(beta)
Carbonate	0.38	1.84	3.22	0.34
Acetate	0.36	1.91	3.25	0.33
Acetate	0.36	2.00	3.19	0.35

**Al_2O_3: RC-172; Calcination: 1300°C/30 min; sintering at 1625°C/10 min.